Preprint
UCRL-JC-135455

Thermodynamics of anisotropic fluids using isotropic potentials

S. Bastea, F.H. Ree

This paper was prepared for submittal to the
International Conference on High Pressure Science and Technology
Honolulu, Hawaii, July 25-30, 1999

August 16, 1999

U.S. Department of Energy
Lawrence
Livermore
National
Laboratory

Thermodynamics of anisotropic fluids using isotropic potentials

Sorin Bastea† and Francis H. Ree*
Lawrence Livermore National Laboratory,
7000 East Avenue, Livermore, CA 94550

We study the effectiveness and limitations of the median potential recipe for mixtures such as $N_2 + O_2$ and $N_2 + CO_2$, that are important in detonation applications. Conversely, we treat effective spherical potentials extracted from Hugoniot experiments (e.g., N_2 and O_2) as median potentials and invert them to extract atom-atom potentials. The resulting non-spherical potentials compare remarkably well with the atom - atom potentials used in studies of solid state properties. Finally, we propose a method to improve the median potential for stronger anisotropic fluids such as CO_2 and its mixtures.

[anisotropic fluids, mixtures, effective spherical potentials, median, atom-atom potentials]

The equilibrium properties of anisotropic molecular fluids can be in principle calculated in a statistical mechanics framework, but the theory is generally too cumbersome for many practical applications. Fortunately, at high densities and temperatures the anisotropy can be 'averaged-out' by means of a density and temperature independent spherical potential (the 'median') that produces reliable thermodynamic data [1,2].

Lebowitz and Percus [2] pointed out some time ago that the success of this approximation can perhaps be understood in terms of a simple theory that treats the asphericity as a perturbation. The idea can be summarized for the more general case of a binary mixture $X+Y$ as follows: If $\phi^{ab}(r,\Omega_1,\Omega_2)$ is the anisotropic potential between molecules of type a and b (a and b run from 1 to 2, where 1 stands for X and 2 for Y) and $\phi_0^{ab}(r)$ the corresponding effective spherical potential, we write $\phi_\gamma^{ab}(r,\Omega_1,\Omega_2) = \phi_0^{ab}(r) + \Delta_\gamma[\phi^{ab},\phi_0^{ab}]$, with $1 \geq \gamma \geq 0$ and $\Delta_0[\phi^{ab},\phi_0^{ab}] = 0$, $\Delta_1[\phi^{ab},\phi_0^{ab}] = \phi^{ab} - \phi_0^{ab}$. Then, if we expand the Helmholtz free energy as

$$F_\gamma = F_0 + \gamma(\partial F/\partial\gamma)|_0 + ... \qquad (1)$$

the condition that the first order correction is zero, $(\partial F/\partial\gamma)|_0 = 0$, imposes a restriction on the potentials $\phi_0^{ab}(r)$. If the concentrations of the X and Y molecules are x and y ($x+y=1$), this translates into

$$\tfrac{1}{2}x^2 \int g_{XX}^0(\mathbf{r_1},\mathbf{r_2})(\partial\Delta_\gamma^{XX}/\partial\gamma)|_0 d\mathbf{r_1}d\mathbf{r_2}d\Omega_1 d\Omega_2 +$$
$$xy \int g_{XY}^0(\mathbf{r_1},\mathbf{r_2})(\partial\Delta_\gamma^{XY}/\partial\gamma)|_0 d\mathbf{r_1}d\mathbf{r_2}d\Omega_1 d\Omega_2 +$$
$$\tfrac{1}{2}y^2 \int g_{YY}^0(\mathbf{r_1},\mathbf{r_2})(\partial\Delta_\gamma^{YY}/\partial\gamma)|_0 d\mathbf{r_1}d\mathbf{r_2}d\Omega_1 d\Omega_2 = 0$$

where g_{ab}^0 are the pair correlation functions for the sphericalized system. The above condition can be enforced independent of density, temperature and concentrations if we require $\int(\partial\Delta_\gamma^{ab}/\partial\gamma)|_0 d\Omega_1 d\Omega_2 = 0$ for all $a's$ and $b's$. The form of the effective spherical potentials, for both like-pair and unlike-pair interactions, depends of course crucially on our choice for Δ_γ^{ab} (in fact only $\partial\Delta_\gamma^{ab}/\partial\gamma)|_0$), which unfortunately is left undefined by the perturbation expansion.

The proposal of Shaw and Johnson [1], which turns out to be the so-called median potential [2], is very successful in predicting the thermodynamics of simple fluids such as N_2 and CO_2 at reasonably high pressures and temperatures [3,4]. The median is defined by using $\partial\Delta_\gamma^{ab}/\partial\gamma)|_0 = sgn(\phi^{ab} - \phi_0^{ab})$, and appears to be the best choice for hard nonspherical potentials [5]. This may explain its success for fluids at high densities, where the hard core contribution is known to be dominant.

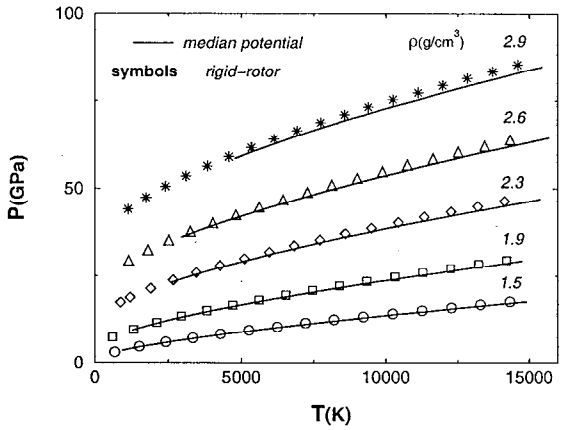

FIG. 1. Test of median potentials for an equimolar N_2+O_2 mixture.

Anisotropic fluids such as N_2, O_2, CO_2 appear as detonation products at high densities and temperatures, generally in mixed form [6]. Therefore, we test the median potential prescription for equimolar mixtures of N_2+O_2 and N_2+CO_2, by comparing the results of MD simulations with rigid rotor atom-atom potentials and with sphericalized potentials in an extended range of densities and temperatures. For the rigid rotor calculations we use atom-atom $exp-6$ potentials,

$$V(r) = \epsilon/(\alpha-6)\{6exp[\alpha(1-r/r^*)] - \alpha(r^*/r)^6\} \qquad (2)$$

The $N-N$ and $O-O$ parameters were extracted from Hugoniot data and for $N-O$ we used the Lorentz-Berthelot rule.

The N_2 and O_2 molecules are moderately anisotropic, with bond lengths $l_{N_2} = 1.098\AA$, $l_{O_2} = 1.207\AA$, and $r_{N_2}^*/l_{N_2} \simeq 0.29$, $r_{O_2}^*/l_{O_2} \simeq 0.35$. We show in Fig. 1 the results of constant density simulations for the N_2+O_2 mixture. The agreement between the rigid rotor and the

median potential results is very good in the range of densities and temperatures studied. This is probably not entirely unexpected as N_2 is a good candidate for sphericalization [3], while O_2 is only slightly more anisotropic, as shown by its r^*/l ratio .

To study the $N_2 + CO_2$ mixture we used a simplified model for the CO_2 molecule [4], that only takes into account the oxygens as centers of force. While this model may not be an accurate predictor of experimental data, it does reproduce the basic anisotropy of the CO_2. The length of the CO_2 molecule is $l_{CO_2} = 2.32\mathring{A}$, and $r^*/l_{CO_2} \simeq 0.70$, which makes it much more anisotropic than either N_2 or O_2. The agreement between the rigid rotor and the sphericalized potential results is limited to smaller particle densities than in the case of $N_2 + O_2$. (Note that a density of $2.3g/cm^3$ for $N_2 + CO_2$ yields approximately the same particle density as $1.9g/cm^3$ in the case of $N_2 + O_2$.)

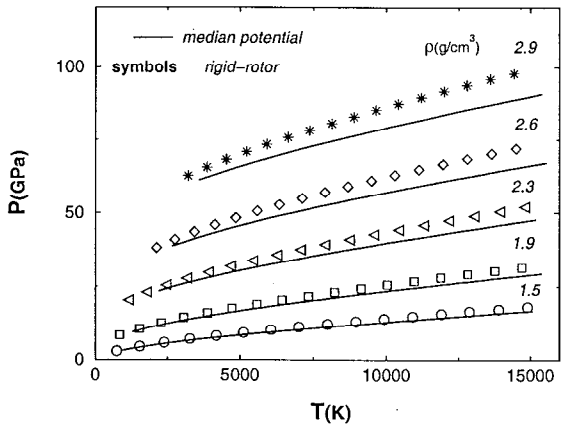

FIG. 2. Test of median potentials for an equimolar $N_2 + CO_2$ mixture.

Perhaps the greatest advantage of the median potential over other effective spherical potentials [7] is the fact that it is independent of density and temperature. The success of the median recipe justifies in fact the analysis and interpretation of experimental shock-wave data on anisotropic fluids in terms of isotropic potentials. These potentials, generally obtained by fitting Hugoniot data [8–11], prove to be reliable in predicting thermodynamic properties at high pressures and temperatures [6].

Given the success of the median, in particular for molecules like N_2 and O_2, we therefore believe that such potentials can be treated like medians and inverted to yield atom-atom potentials. We carried out this task for N_2 and O_2, by assuming an $exp-6$ form for the $N-N$ and $O-O$ interactions. This simple functional form turns out to be sufficient for extracting with very good accuracy atom-atom potentials from the N_2-N_2 and O_2-O_2 intermolecular interactions. We show in Fig. 2 our $O-O$ potential, together with an $O-O$ potential used to model solid state data of molecular O_2 at high pressures [12]. The agreement is very good, showing that unique sets of atom-atom potentials should perhaps be sufficient to describe the thermodynamic properties of simple anisotropic molecular systems in both fluid and solid states.

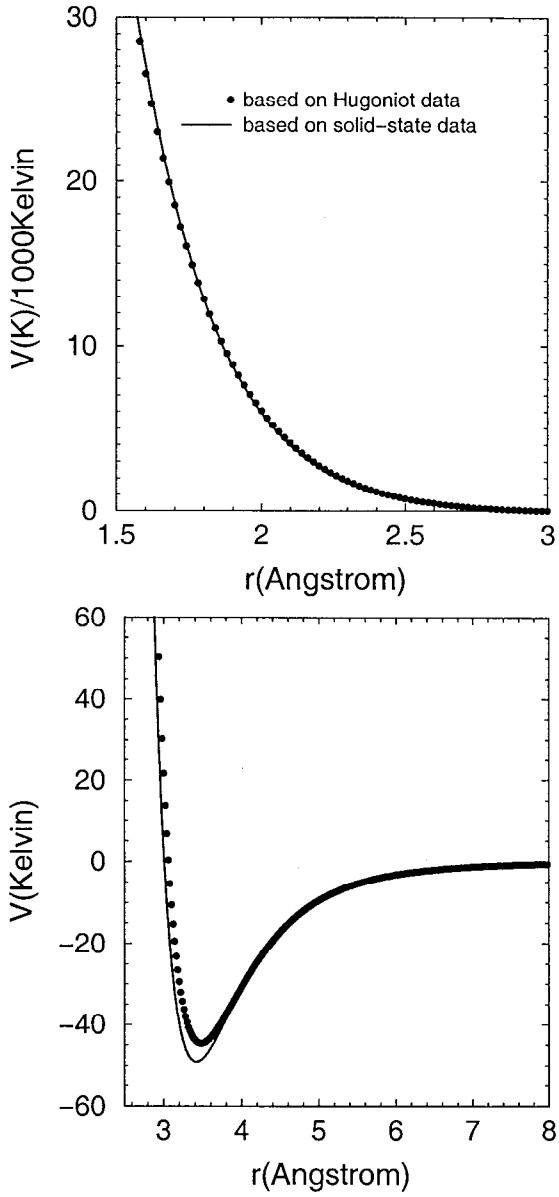

FIG. 3. $O-O$ atom-atom potential based on shock and solid phase data; repulsive region (top) and attractive region (bottom).

The lower accuracy of the median for $N_2 + CO_2$ mixtures, in particular at higher temperatures, can be largely traced back to its performance in the case of pure CO_2 - see Fig. 3. Nevertheless, given the general success of the median prescription, we would like to improve it in a systematic way. Unfortunately, the basis for the median construction is rather heuristic [2,5], and seems to defy a full explanation [13,14].

To make progress, we turn to the observation that the

median minimizes the sum of absolute deviations [7,15] $\int d\Omega_1 \int d\Omega_2 |\phi(r,\Omega_1,\Omega_2) - \phi_0(r)|$. We interpret this as an effective way of constructing an isotropic interaction between two *isolated* molecules.

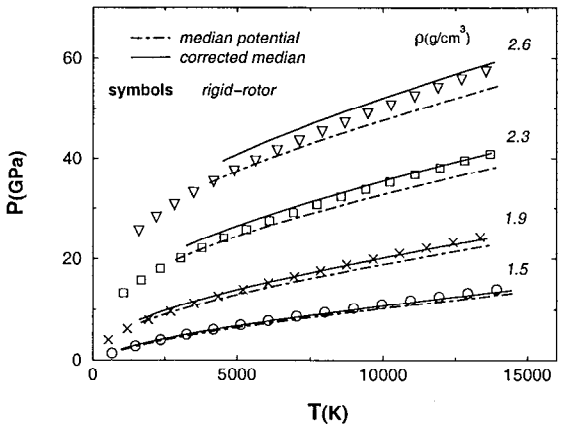

FIG. 4. Non-spherical versus sphericalized potentials for CO_2; comparison between median and corrected median (see text).

However, at high densities, in particular for hard bodies, the presence of a third molecule will restrict the configurations available to the first two molecules. We take this into account in an heuristic way by using a relatively small number of positions for the third molecule; details will be reported elsewhere [16]. The new potential, that we call corrected median, yields results as shown in Fig. 3. We believe that they are promising, as they improve the pressure predictions, in particular at high temperatures. Further refinements and the testing of the procedure for mixtures are underway [16].

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

† Electronic address: bastea2@llnl.gov
* Electronic address: ree1@llnl.gov

[1] M. S. Shaw, J. D. Johnson and B. L. Holian, Phys. Rev. Lett. **50**, 1141, (1983).
[2] J. L. Lebowitz and J. K. Percus, J. Chem. Phys. **79**, 443, (1983).
[3] J. D. Johnson, M. S. Shaw and B. L. Holian, J. Chem. Phys. **80**, 1279, (1984).
[4] J. D. Johnson and M. S. Shaw, J. Chem. Phys. **83**, 1271, (1985).
[5] G. O. Williams, J. L. Lebowitz and J. K. Percus, J. Chem. Phys. **81**, 2070, (1984).
[6] F. H. Ree, J. Chem. Phys. **81**, 1251, (1984).
[7] J. K. Percus, Ann. NY Acad. Sci. **452**, 67, (1985).
[8] M. Ross, J. Chem. Phys. **86**, 7110, (1987).
[9] D. C. Hamilton, W. J. Nellis, A. C. Mitchell, F. H. Ree and M. van Thiel, J. Chem. Phys. **88**, 5042, (1988).
[10] W. J. Nellis, H. B. Radousky, D. C. Hamilton, A. C. Mitchell, N. C. Holmes, K. B. Christianson and M. van Thiel, J. Chem. Phys. **94**, 2244, (1990).
[11] D. C. Hamilton and F. H. Ree, J. Chem. Phys. **90**, 4972, (1989).
[12] R. D. Etters, A. Helmy and K. Kobashi, Mat. Res. Soc. Symp. Proc. Vol. **22**, 103, (1984).
[13] D. MacGowan, D. B. Nicolaides, J. L. Lebowitz and Chul-Kyu Choi, Mol. Phys. **58**, 131, (1986).
[14] D. MacGowan, J. D. Johnson and M. S. Shaw, J. Chem. Phys. **82**, 3765, (1985). 103, (1984).
[15] D. MacGowan, E. M. Waisman, J. L. Lebowitz and J. K. Percus, J. Chem. Phys. **80**, 2719, (1984).
[16] S. Bastea and F. H. Ree, in preparation.